(51) International Patent Classification 6:		(11) International Publication Number:	**WO 97/38964**
C07C 67/38, 69/017, 69/24, C10M 105/34	A1	(43) International Publication Date:	23 October 1997 (23.10.97)

(54) Title: PROCESS FOR THE CARBONYLATION OF ETHYLENICALLY UNSATURATED COMPOUNDS

(57) Abstract

The invention provides a process for the carbonylation of ethylenically unsaturated compounds by reaction thereof with carbon monoxide and a coreactant in the presence of a catalyst system obtainable by combining (a) a source of a Group VIII metal cation, (b) a phosphine, arsine or stibine compound acting as a ligand; and (c) a source of anions, other than halide anions, carried out in the presence of substoichiometric amounts of halide anions and/or - in case of a coreactant other than an aromatic alcohol - in the presence of a phenolic promoter. It also provides novel alkylphenol esters that find use as synthetic lubricant.

PROCESS FOR THE CARBONYLATION OF
ETHYLENICALLY UNSATURATED COMPOUNDS

The invention relates to a process for the carbonyla-
tion of ethylenically unsaturated compounds by reaction
with carbon monoxide and a coreactant in the presence of
a homogeneous catalyst system comprising a source of
Group VIII metal cation and a ligand. It also relates to
alkylphenol esters so produced and to the use of
alkylphenolesters in automotive and industrial
applications.

Carbonylation reactions are known in the art. For
instance, in EP-A-0,495,547 several examples are dis-
closed wherein olefins are converted into (thio)esters,
acids, anhydrides, and amides, etc., depending on the
nature of the coreactant. Similarly, in WO 94/18154, a
process modification is disclosed, based on the presence
of an amine, whereby the rate of the carbonylation
reaction as described in EP-A-0,495,547 is increased.

Whilst the process disclosed in WO 94/18154 provides
the desired product in better yield and with greater
selectivity than in EP-A-0,495,547, further improvement
remains desirable. Indeed, there still remain instances
where reaction is slow to proceed if at all.

The present invention aims at providing a process
with increased reaction rate, without impeding other
factors such as selectivity or catalyst stability.
Surprisingly, it has now been found that by inclusion
into the catalyst system of substoichiometric amounts of
halide anions, and/or -in case of a coreactant other than
an aromatic alcohol- by the presence of a phenolic com-
pound, the catalyst activity is substantially increased.

Accordingly, the invention provides a process for the
carbonylation of ethylenically unsaturated compounds by

reaction thereof with carbon monoxide and a coreactant in the presence of a catalyst system obtainable by combining (a) a source of a Group VIII metal cation (b) a phosphine, arsine or stibine compound acting as a ligand; and (c) a source of anions, other than halide anions, carried out in the presence of substoichiometric amounts of a halide anion and/or -in case of a coreactant other than an aromatic alcohol- in the presence of a phenolic promoter.

It is believed that the carbonylation reactions proceed under the influence of an active catalyst system containing one or more Group VIII metal cations, in complex coordination with the ligand, the ethylenically unsaturated compound and the halide anion and/or the phenolic promoter.

The halide anion can be a chloride, bromide, iodide, or fluoride anion. From a commercial point of view, based on price and availability, the chloride is preferred. From a technical point of view, based on its greater promoting effect and the linearity of the carbonylation products, the iodide anion is preferred.

Substoichiometric in this specification means that less halide anions are present than required to neutralise the Group VIII metal cations. Preferably, the molar ratio of dissociated halide anions versus Group VIII metal cations is less than 2:1, for instance from 0.02:1 to 1:1, per mole of cation. The ideal ratio depends on the liquid medium and may be easily found by those skilled in the art. Suitable sources of the halide anion include both hydrogen halides, e.g., HCl, HBr and HI, quaternary ammonium or phosphonium halides, e.g., triphenylmethylphosphonium chloride and metal halides, e.g., NaCl, $MgBr_2$, $ZnCl_2$, ZnI_2, LiBr, RbCl, CsCl, CsI, MgI_2 and CuCl, in particular alkali or earth alkaline metal halides.

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The phenolic promoter is an aromatic compound having
one or more hydroxyl groups attached to the aromatic
backbone of the compound. Typically, the aromatic
backbone is a 6-membered ring, which may be part of a
larger fused (aromatic) ring system. Examples of such
aromatic compounds include 3-hydroxypyridine, 3- or 6-
quinolinol, 1- or 2-hydroxynaphthalene (α- or β-
naphthol), o,o'-, m,m'- or p,p'-biphenol, 2,2-di(p-
phenylol)propane (DPP), etc. Suitably, it is a 6-membered
ring composed of carbon atoms only. More suitably, the
aromatic backbone is a benzene ring, optionally having
one or more inert groups, such as alkyl groups of up to
20 carbon atoms, attached thereon. For instance, the
phenolic promoter may be 3,5-dimethoxyphenol, hydroqui-
none, or phenol, etc. Preferably, the phenolic promoter
is DPP or phenol. The use of the phenolic promoter has
been found particularly beneficial in an amount of up to
40% by weight, based on the total weight of reactants,
optional solvent and the catalyst system. Preferably, it
is used in an amount of 10 to 20 %wt.

It will be understood that the phenolic promoter
cannot at the same time partake in the carbonylation
reaction as coreactant. Therefore, in order for the
phenolic promoter to function as promoter, another
compound must be present to act as coreactant.

Preferably, the carbonylation process is carried out
in the presence both of the phenolic promoter and the
halide anion.

The carbonylation reaction is conveniently carried
out at moderate temperatures. Accordingly, the process is
suitably carried out at a temperature in the range of
from 30 to 200 °C, eg from 100 to 200°C. Preferred
temperatures are in the range of from 50 to 180 °C. The
reaction pressures may also vary widely. For instance,
the reaction can be carried out at a pressure in the

range of from 1 to 200 bar gauge, pressures in the range
of from 5 to 60 bar g being preferred.

Carbon monoxide is preferably supplied in molar
excess over the ethylenically unsaturated compound and
the coreactant. In addition, the ethylenically
unsaturated compound and the coreactant are suitably
supplied in a molar ratio in the range of from 10:1 to
1:10, preferably in the range of from 5:1 to 1:5, more
preferably in the range of from 2:1 to 1:2.

In the present specification, Group VIII metals
(referring to the Periodic Table of the Elements as
disclosed in the 61st ed. of the Handbook of Chemistry
and Physics) comprise the elements Fe, Co, Ni, Ru, Rh,
Pd, Os, Ir and Pt. Preferably the Group VIII metal is a
platinum group metal, i.e., Ni, Pd or Pt. Of these,
palladium is most preferred.

Examples of suitable sources of the cation are salts,
such as salts of the Group VIII metal and nitric acid,
sulphuric acid, carboxylic acids having up to 12 carbon
atoms in the carboxylate group or sulphonic acid; and
metal complexes, e.g., with carbon monoxide or acetyl-
acetonate. Palladium(II) acetate is an example of a
suitable source of the preferred cation.

Regarding the phosphine, arsine or stibine compound
acting as ligand, monodentate ligands such as triphenyl-
phosphine, etc., may be used. However, preference is
given to bidentate ligands containing a second atom that
coordinates with the cation, selected from trivalent N,
P, As or Sb atoms. Suitably, these bidentate ligands have
an organic bridging group that contains from 1 to 5 atoms
in the bridge between the two coordinating atoms. One
example of such a bidentate ligand is diphenyl-
(2-pyridyl)arsine.

Preferred bidentate ligands are compounds of the
formula $R^1R^2M^1-R-M^2R^3R^4$, wherein M^1 and M^2 independently

are P, As or Sb, R represents a bivalent substituted or
non-substituted bridging group containing from 1 to 5
atoms in the bridge, R^1 and R^2 together are a substituted
or non-substituted bivalent group whereby the two free
valencies are linked to M^1, and R^3 and R^4 together are a
substituted or non-substituted bivalent group whereby the
two free valencies are linked to M^2 or R^3 and R^4 inde-
pendently represent a substituted or unsubstituted
hydrocarbyl group.

Regarding the preferred bidentate ligands, M^1 and M^2
preferably both represent phosphorus atoms. The bivalent
bridging group R typically is an organic group, inclusive
of organometallic groups such as ferrocylene as in
WO 95/06027 or ortho-anellated annular systems as in
WO 95/30680, connecting the atoms M^1 and M^2 through
carbon atoms. Usually all bridging atoms are carbon
atoms, optionally with hetero-atoms (other than H or C)
attached thereto. Preferably, R represents an alkylene
group containing from 1 to 3 carbon atoms in the bridge,
suitably 2 or 3, in particular an ethylene group or a
propylene group. In the preparation of alkylphenol
esters, R ideally represents a propylene group.

The bivalent substituted or non-substituted group,
represented by R^1 together with R^2, preferably contains
from 5 to 9 atoms, preferably 8 atoms. Examples of
suitable bivalent groups include 1,6-hexylene, 1,6-
heptylene, and 1,5-octylene. Together with M^1, this group
forms a phosphacycloalkyl group. Preferably, R^1 together
with R^2 represent a bivalent substituted or non-
substituted cyclic group. Together with M^1, this
preferred group forms a phosphabicycloalkyl group.
Examples of suitable bivalent cyclic groups are
1,4-cyclohexylene, 1,4-cycloheptylene, 1,2-cyclooctylene,
1,4-cyclooctylene, 1,5-cyclooctylene and 2-methyl-1,5-
cyclooctylene groups.

R^3 and R^4 may independently represent any substituted or unsubstituted hydrocarbyl group, such as alkyl, aryl, alkaryl or aralkyl groups. Preferably, R^3 and R^4 together have the same meaning as R^1 together with R^2.

Suitable substituents in the case that any of R, or R^1 to R^4 is substituted may be selected from the group consisting of halogen atoms, and cyano, alkoxy, amino and alkylamino groups. The alkyl groups in the alkoxy and alkylamino groups preferably each contain from 1 to 4 carbon atoms.

Particularly preferred bidentate ligands are the [3,3,1] and [4,2,1] isomers of 1,2-P,P'-bis(9-phosphabicyclononyl)ethane, 1,2-P,P'-bis(dimethyl-9-phosphabicyclononyl)ethane, 1,3-P,P'-bis(9-phosphabicyclononyl)propane, 1,3-P,P'-bis(dimethyl-9-phosphabicyclononyl)propane.

For the preparation of the bidentate ligands, reference is made to known techniques, for example the method disclosed in British patent specification No. 1,127,965 and Canadian patent specification No. 2,086,285.

The catalyst systems used in the process of the invention are further based on a source of anions other than halide anions, i.e., component (c). It is believed that the size of the anion and the distribution of electric charge in the anion significantly contribute to the stability of the catalyst system. Suitably, acids are used as the source of anions, or the salts thereof. Preferably, anions are used that are the conjugated base of acids having a pKa (measured at 18 °C in water) of less than 3, preferably less than 2. The anions derived from these acids are non-coordinating or weakly coordinating with the Group VIII metal cation, by which is meant that little or no covalent interaction occurs between the anion and the cation. Catalysts based on

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these anions exhibit a substantially improved activity.

Suitable anions include anions derived from Bronsted acids, such as from phosphoric acid and sulphuric acid, and in particular from sulphonic acids and (halogenated) carboxylic acids, such as trifluoroacetic acid, 2,6-dichlorobenzoic acid, and 2,6-bis(trifluoromethyl)-benzoic acid or trifluoroacetic acid. Anions derived from sulphonic acids are particularly preferred, for example methanesulphonic acid, trifluoromethanesulphonic acid, tert-butanesulphonic acid, p-toluenesulphonic acid and 2,4,6-trimethylbenzenesulphonic acid.

Also, complex anions are suitable, such as the anions generated by a combination of a Lewis acid such as BF_3, $B(C_6F_5)_3$, $AlCl_3$, SnF_2, $Sn(CF_3SO_3)_2$, $SnCl_2$ or $GeCl_2$, with a protic acid, preferably having a pKa of less than 5, such as a sulphonic acid, e.g. CF_3SO_3H or CH_3SO_3H or a hydrohalogenic acid such as HF or HCl, or a combination of a Lewis acid with an alcohol. Examples of such complex anions are BF_4^-, $SnCl_3^-$, $[SnCl_2.CF_3SO_3]^-$ and PF_6^-.

When an organic or inorganic base is present, e.g., as further catalyst promoter, anions derived from acids having a pKa in the range of 6 to 3 may also be used. Examples thereof include carboxylic acids.

The quantity in which the catalyst system is used, is not critical and may vary within wide limits. Usually amounts in the range of from 10^{-8} to 10^{-1}, preferably in the range of from 10^{-7} to 10^{-2} mole atom of component (a) per mole of ethylenically unsaturated compound are used.

For the preparation of the catalyst systems of the invention, the amount of ligand is generally applied in some excess of the amount of the Group VIII metal cation, expressed as moles of ligand per mole atom of the cation. Typically the amount of ligand is selected such that per mole atom of the cation, in the range of from 0.5 to 10 moles of ligand are present. However, for the preferred

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catalyst system the active species is believed to be based on an equimolar amount of bidentate ligand per mole cation. Thus, the molar amount of bidentate ligand per mole of cation is preferably in the range of from 1 to 3,
5   more preferably in the range of from 1 to 2. In the presence of oxygen, slightly higher amounts may be beneficial. The amount of the anion source may range from 0.5 to 15, preferably from 1 to 8 moles per mole of cation.

10   If desired, the reaction may be performed in the presence of a further catalyst promoter, such as an organic or inorganic base. Suitably, an amine is used. The amine is typically a cyclic amine or a tertiary amine, for example a trialkylamine. A preferred further
15   catalyst promoter is triethylamine. The amine may be used in large amounts. Suitable amounts include up to 1000, e.g., from 1 to 20 moles per mole of cation. In particular in the carbonylation of (cyclo)alkadienes, and or the carbonylation with (substituted) phenols as
20   coreactant, the presence of a further catalyst promoter has been found very beneficial.

In the process of the invention, the starting materials and the formed carbonylation products may act as reaction diluent. Hence, the use of a separate solvent
25   is not necessary. Conveniently, however, the carbonyla- tion reaction may be carried out in the additional presence of a solvent. As such, saturated hydrocarbons, e.g. paraffins and isoalkanes are recommended and furthermore ethers such as 2,5,8-trioxanonane (diglyme),
30   diethylether and anisole, sulphones such as sulpholane, and aromatic hydrocarbons such as toluene.

The ethylenically unsaturated compound may have one or more double bonds and is preferably an olefin having from 2 to 30 carbon atoms per molecule. The unsaturated
35   bond(s) may be internal or, preferably, terminal.

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Particularly preferred are olefins having from 2 to
22 carbon atoms per molecule, such as ethene, propene,
1-butene, 1-hexene, 1-octene, 1-dodecene and
1-octadecene.

In the ethylenically unsaturated compound one or more
hydrogen atoms may have been substituted by other atoms,
such as halogen atoms or by groups of atoms, such as
hydroxyl groups, cyano groups, such as methoxy or ethoxy
groups, or amino groups such as dimethyl- and diethyl-
amino groups.

Another preferred category of ethylenically unsatu-
rated compounds, consists of unsaturated esters of
carboxylic acids and esters of unsaturated carboxylic
acids. For example, the starting material may be a vinyl
ester of a carboxylic acid such as acetic acid or
propanoic acid, or it may be an alkyl ester of an
unsaturated acid, such as the methyl or ethyl ester of
acrylic acid or methacrylic acid.

A further preferred category of ethylenically
unsaturated compounds, consists of cycloalkadienes, which
will ordinarily refuse carbonylation. For example, the
starting material may be dicyclopentadiene or norborna-
diene, to give diesters, diamides or diacids, etc., which
may find use as monomer in polymerization reactions.

Suitable coreactants in the process of the invention
include compounds comprising a nucleophilic moiety and a
mobile hydrogen atom.

Preferred nucleophilic compounds include: water and
alcohols, e.g., monohydric alcohols, such as methanol,
ethanol, isopropanol and 1-butanol, and polyhydric alco-
hols, such as ethyleneglycol, 1,4-butanediol and
glycerol; thiols; primary or secondary (poly)amines or
amides, such as diethylamine, N,N-dimethyl ethylene-
diamine; aromatic alcohols and carboxylic acids, for
example acetic acid, pivalic acid and propanoic acid.

Monohydric alcohols having from 1 to 6 carbon atoms per molecule and dihydric alcohols having from 2 to 6 carbon atoms per molecule are preferred.

1-Butanol, methanol and 1,4-butanediol are especially preferred. The use of these compounds as coreactants enables the production of valuable carbonylation products, such as methyl propanoate, butyl propanoate and 1,4-diacyloxy butanes. These compounds are of commercial interest and may be used as solvents and in flavouring compositions and perfumes.

Another preferred class of coreactants is composed of alkylphenols, wherein one or more alkyl groups of up to 30, typically 4 or 6 to 22 carbon atoms are attached to the phenol molecule. Carbonylation of these coreactants produces alkylphenyl esters. Certain of these alkylphenyl esters may find use as synthetic lubricants in industrial application, but in particular in automotive engines, as they exhibit a very low volatility combined with a low viscosity and a high oxidation stability. These characteristics give the alkylphenyl esters a significant advantage over existing lubricants when considering two important requirements for future lubricants: increasing fuel economy and lowering emissions. Besides, they exhibit excellent hydrolytic stability, good cleanliness performance and good elastomer compatibility.

From Japanese patent specification no. 2-292395A, esters of alkyphenols and monobasic acids are proposed as component base oils for lubricant compositions. The alkyl phenol ester proposed have the formula
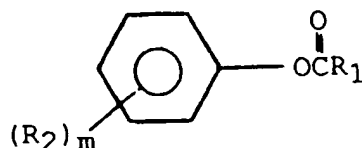
in which m is 0 to 2, R_1 is hydrocarbon eg alkyl, and R_2 is alkyl of 1 to 8 carbon atoms. No specific example of

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such an ester is disclosed, nor are any lubricant
properties for such compounds specified. It has now been
found that C_{1-8} alkylphenol esters have unsuitable
properties as lubricants whereas similar alkyl phenol
esters but with a higher carbon-containing alkyl
substituent surprisingly show significantly better
volatility, VI and pour point properties.

Thus, the invention also provides novel alkylphenyl
esters of the general formula

$$R'_n C_6 H_{(5-n)} OC(=O)R'' \qquad (I)$$
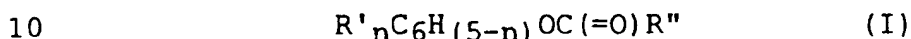
wherein R' is an alkyl group of from 10 to 30 carbon
atoms, suitably of from 10 or 12 to 22, preferably from
10 to 20, more preferably from 12 to 20, especially from
14 to 18, carbon atoms, n is an integer of 1 to 5,
typically 1 or 2, and R" is an alkyl group of from 1 to
30 carbon atoms, suitably of from 4 to 22, preferably 6
to 20, more preferably 6 to 15, especially 8 to 12,
carbon atoms. Preferably, n is 1, and R' together with R"
preferably have from 20 to 40 carbon atoms. More
preferably, the number of carbon atoms in R' is equal to
or preferably larger than to the number of carbon atoms
in R".

An alkyl group R' or R" may be a straight chain or
branched chain alkyl group. The starting alkylphenol is
suitably prepared by alkylation of the phenol. For
instance, they may be prepared by alkylation of a phenol
with an alpha or internal olefin, e.g., such as an alpha
olefin having from 14 to 18 carbon atoms. The novel
alkylphenol esters may also be prepared through
esterification, e.g., by reaction of the alkylphenol with
the carboxylic acid or corresponding acid chloride by
conventional procedures, eg preferably at reflux, in an
organic solvent, if necessary, and using an acid
catalyst, for example methane sulphonic acid.

The invention further provides the use of the

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alkylphenyl esters of formula I as synthetic lubricants,
for instance in automotive applications. In particular
the alkylphenyl esters wherein R' together with R" have
from 20 to 40 carbon atoms exhibit attractive properties
regarding viscosity, oxidative stability and volatility.
Those wherein the number of carbon atoms in R' is equal
to or preferably larger than the number of carbon atoms
in R" can exhibit an attractive, low pour point.
Oxidative stability and pour point may be further
improved by the presence of branched alkyl groups in
either R' (resulting from alkylation with an internal or
branched olefin) or R" (resulting from carbonylation of
an internal or branched olefin).

Finally, in accordance with the present invention
there is also provided a lubricating oil composition
comprising as a base fluid an alkylphenol ester as
mentioned above. In the lubricating oil composition, the
alkylphenol ester may be present in an amount of at least
2% by weight, preferably at least 10% w/w, more prefer-
ably at least 40% w/w of the total base fluid. It may be
present in an amount up to 100% w/w, preferably up to 90%
w/w, more preferably up to 75% w/w on the same basis. It
should be understood, however, that the amount of alkyl-
phenol ester may vary with the price-performance aimed
at. Furthermore, in the lubricating oil composition
according to the present invention, the balance of the
total base fluid is preferably a base oil of mineral or
synthetic origin.

Suitable additives with which the compounds of the
present invention may be used for engine oil application
may include one or more extreme pressure/anti-wear
agents, for example zinc salts such as zinc dialkyl or
diaryl phosphorodithioates (at a concentration giving
from 0 to 0.15% w/w phosphorus in the lubricating oil
composition); one or more overbased metal-containing

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detergents such as calcium or magnesium alkyl salicylates
or alkylarylsulphonates (present at total detergent
concentration in the lubricating oil composition from 0
to 20% w/w); one or more detergents such as phenates and
5   phenate/sulphonate mixtures (present at total detergent
concentration in the lubricating oil composition from 0
to 20% w/w); one or more ashless dispersant additives
such as reaction products of polyisobutenyl succinic
anhydride and an amine or ester (present at total
10   dispersant active matter concentration in the lubricating
oil composition from 0 to 20% w/w); optionally one or
more primary antioxidants, for example hindered phenols
or amines (present at concentrations in the lubricating
oil composition from 0 to 5% w/w). Other supplementary
15   additives, for example anti-rust or friction-modifying
additives may optionally be present. Viscosity Index
improving polymers may optionally be present at polymer
concentrations from 0 to 20% w/w. Pour point depressing
additives may optionally be present at concentrations
20   from 0 to 5% w/w.

     The balance of base oil in the lubricating oil
composition may be a base oil of mineral or synthetic
origin. Base oils of mineral origin may be mineral oils,
for example produced by solvent refining or hydro-
25   processing. Base oils of synthetic origin may typically
be mixtures of C_{10-50} hydrocarbon polymers, for example
liquid polymers of alpha-olefins. They may also be
conventional esters, for example polyol esters. The base
oil may also be a mixture of these oils. Preferably the
30   base oil is that of mineral origin sold by the Royal
Dutch/Shell Group of Companies under the designations
"HVI" (trade mark) or, most preferably, the synthetic
hydrocarbon base oils sold by the Royal Dutch/Shell Group
of Companies under the designation "XHVI" (trade mark).
35   The invention will now be further described in the

following examples, however, without restricting its scope. All experiments were carried out in a magnetically stirred 250 ml autoclave unless otherwise indicated. The abbreviations used in the Tables have the following

5   meanings:

BCPE = 1,2-P,P'-bis(9-phosphabicyclo[3,3,1 or 4,2,1]nonyl)ethane;

BCPP = 1,3-P,P'-bis(9-phosphabicyclo[3,3,1 or 4,2,1]nonyl)propane;

10   MSA = methanesulphonic acid;

DPP = 2,2-di(p-phenylol)propane.

Example 1 (Comparative)

The autoclave was charged with 20 ml of butanol, 40 ml of butyl propanoate (solvent), 0.25 mmol of palla-

15   dium(II) acetate, 0.6 mmol of BCPE, 0.5 mmol of MSA and 5 ml of triethylamine. After being flushed, the autoclave was pressurised with carbon monoxide and ethene to a partial pressure of 15 bar and 10 bar respectively. Next, the reactor was sealed. The contents of the autoclave

20   were heated to a temperature of 125 °C and maintained at that temperature for 2 hours. After cooling, a sample was taken from the contents of the autoclave and analysed by Gas Liquid Chromatography.

Ethene was fully converted with 100% selectivity into

25   butyl propanoate at an average rate of 300 mol per mole Pd per hour (mol/mol.hr). Similar results were found in the presence of 1 ml triethylamine.

Example 2

The experiment of Example 1 was repeated, however, in

30   the presence of 0.25 mmol HCl.

Ethene was now fully converted with 100% selectivity into butyl propanoate at an average rate of 1200 mol/mol.hr.

Example 3

35   The experiment of Example 1 was repeated, however, in

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the presence of 2 mmol propanoic acid instead of MSA and in the presence of 10 g DPP.

Ethene was now fully converted with 100% selectivity into butyl propanoate at an average rate of 1200 mol/mol.hr.

When phenol is used instead of DPP, an average rate was found of 1200 mol/mol.hr.

Example 4

The experiment of Example 1 was repeated, however, in the presence of 0.25 mmol HCl and 5 g phenol.

Ethene was now fully converted with 100% selectivity into butyl propanoate at an average rate of 4000 mol/mol.hr. When 10 g of phenol were used, the average rate increased to 8000 mol/mol.hr. An average rate of 8000 mol/mol.hr was also found when 10 g of DPP instead of phenol, and triphenylmethylphosphonium chloride instead of HCl were used.

Example 5

The experiment of Example 1 was repeated, however, without triethylamine and 1 mmol of propanoic acid instead of MSA, and in the presence of 0.25 mmol HCl and 10 g phenol.

Ethene was now fully converted with 100% selectivity into butyl propanoate at an average rate of 7000 mol/mol.hr. When 2 ml of triethylamine were added, the average rate increased to 8000 mol/mol.hr.

Example 6

The autoclave was charged with 20 ml 1-octene, 15 ml N,N-dimethyl-1,3-propanediamine, 40 ml toluene, 0.25 mmol of palladium(II) acetate, 0.6 mmol BCPE, 0.5 mmol MSA, 0.25 mmol NaCl and 10 g of α-naphthol. After being flushed, the autoclave was pressurised with 20 bar carbon monoxide. Next, the reactor was sealed. The contents of the autoclave were heated to 145°C and maintained at that temperature for 5 hours. After cooling, a sample was

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taken from the contents of the autoclave and analysed by GLC.

The product, (N,N-dimethyl-3-aminopropyl)nonanamide, was formed with a linearity of 92%. An olefin conversion of 50% was reached, corresponding to an average rate of 300 mol/mol.hr.

Example 7

Example 6 was repeated, however, with NaI instead of NaCl. Besides, the contents of the autoclave were now heated for 1 hour.

The product was formed with a linearity of 97%, whereas an olefin conversion of 60% was reached. This corresponds to an average rate of 1500 mol/mol.hr.

Example 8

Example 7 was repeated, however, at 125 °C instead of 145 °C. The contents of the autoclave were now heated for 1.5 hours.

The product was now formed with a linearity of 98.5%, whereas an olefin conversion of 80% was reached. This corresponds to an average rate of 1000 mol/mol.hr.

Example 9

The autoclave was charged with 20 ml 1-octene, 15 ml 2-aminoethanol, 40 ml diglyme, 0.25 mmol of palladium(II) acetate, 0.6 mmol BCPE, 0.5 mmol MSA, 0.25 mmol NaI and 5 g of phenol. After being flushed, the autoclave was pressurised with 20 bar carbon monoxide. Next, the reactor was sealed. The contents of the autoclave were heated to 175 °C and maintained at that temperature for 1 hour. After cooling, a sample was taken from the contents of the autoclave and analysed by GLC.

The product, (2-ethylol)nonanamide, was formed with a linearity of 97%. An olefin conversion of 60% was reached, corresponding to an average rate of 1500 mol/mol.hr.

Example 10

Example 14

The autoclave was charged with 5 ml dicyclopentadiene (DCPD), 40 ml methanol, 0.25 mmol of palladium(II) acetate, 0.6 mmol BCPE, 0.5 mmol MSA, 0.25 mmol NaI, 2 ml triethylamine and 5 g of phenol. After being flushed, the autoclave was pressurised with 20 bar carbon monoxide. Next, the reactor was sealed. The contents of the autoclave were heated to 155 °C and maintained at that temperature for 10 hours. After cooling, a sample was taken from the contents of the autoclave and analysed by GLC.

The product was analysed to be composed for 64% of diesters and 36% of monoesters (by mole). The product was formed at 100% DCPD conversion and an average rate of 30 mol/mol.hr.

At a temperature of 165 °C, the diester content increased to 70%, and the average rate to 100 mol/mol.hr.

Example 15

Example 14 was repeated, however, using 10 g phenol (155 °C). The diester content increased to 80%, and the average rate to 150 mol/mol.hr.

Example 16

Example 14 was repeated, however, using 10 g β-naphthol or 3,5-dimethoxyphenol (155 °C). The diester content in each experiment increased to 84%, and the average rate to 200 mol/mol.hr.

Example 17

A hexadecylphenol was prepared by alkylating phenol with 1-hexadecene in the presence of 2% by weight of an acidic zeolite as catalyst.

The autoclave was charged with 11 ml 1-octene, 41.75 g of the hexadecylphenol, 26 g sulpholane, 0.25 mmol of palladium(II) acetate, 0.6 mmol BCPP, 0.5 mmol MSA, 0.10 mmol HCl and 1.65 ml triethylamine. After being flushed, the autoclave was pressurised with

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17.7 bar carbon monoxide. Next, the reactor was sealed. The contents of the autoclave were heated to 140 °C and maintained at that temperature for 6 hours. After cooling, a sample was taken from the contents of the autoclave and analysed by GLC.

Hexadecylphenyl nonanoate was formed at 61.5% hexadecylphenol conversion with 100% selectivity at an average rate of 187 mol/mol.hr.

Example 18

A C_{14-18}-alkylphenol was prepared by alkylating phenol with a mixture of C_{14-18}-1-alkenes in the presence of 2% by weight of an acidic zeolite as catalyst.

The autoclave was charged with 18.3 ml 1-dodecene, 39.7 g (122 mmol) of the C_{14-18}-alkylphenol, 25 g sulpholane, 0.26 mmol of palladium(II) acetate, 0.66 mmol BCPP, 0.10 mmol HCl and 1 ml triethylamine. After being flushed, the autoclave was pressurised with 16.4 bar carbon monoxide. Next, the reactor was sealed. The contents of the autoclave were heated to 125 °C and maintained at that temperature for 6 hours. After cooling, a sample was taken from the contents of the autoclave and analysed by GLC.

The C_{14-18}-alkylphenyl tridecanoate was formed at 76.2% alkylphenol conversion with 100% selectivity at an average rate of 188 mol/mol.hr.

Example 19 - hexadecylphenyl dodecanoate

In a 0.5 litre 3-necked flask equipped with a Dean and Stark apparatus were placed 120 g (0.6 mol) dodecanoic acid, 63.6 g (0.2 mol) hexadecyl phenol and 80 g of xylene. The mixture was heated gently until the dodecanoic acid had melted. Next 1 g of methanesulphonic aicd was added and the mixture was heated to reflux (170°C) while water was removed continuously. After 5 hours a 99% conversion of alkylphenol was reached. Xylene was removed on a rotary evaporator at 100°C/10 mbar. The

excess dodecanoic acid was removed on a wiped film
evaporator at 120°C/0.02 mbar, while the remaining
alkylphenol ester was purified by a final wiped film
evaporator distillation at 220°C/0.01 mbar, yielding 89%
of isolated ester.

Example 20 - C14/16/18-alkylphenyl octanoate

In a 10 l round-bottomed glass reactor connected to a
vacuum pump and equipped with a nitrogen gas inlet (50
l/h), a mechanical stirrer, a temperature sensor, a
pressure sensor and a Dean and Stark apparatus were placed
3996 g (27.75 mol) of octanoic acid and 3010 g (0.26 mol)
of mixed C14/16/18 alkylphenol. The mixture was stirred
and purged with nitrogen and subsequently 44.31 g (0.46
mol) of methanesulphonic acid was added. The pressure in
the reactor was lowered to 85-73 mbar and the contents of
the flask were heated to 164-168°C. After about 6 hours
134 g of water were collected in the Dean and Stark trap.
The nitrogen pressure was raised to 1 bar and the mixture
was continuously purged with nitrogen and allowed to cool
to room temperature. The excess of octanoic acid was
removed by passing the product twice through a wiped film
evaporator at 150°C, 0.1 mbar. Subsequently, the product
was filtered to give 3914 g (94% yield) of mixed
C14/16/18-alkylphenyl octanoate.

Example 21 - C14/16/18-alkylphenylnonanoate

In a 10 l round-bottomed glass reactor connected to a
vacuum pump and equipped with a nitrogen gas inlet (50
l/hr), a mechanical stirrer, a temperature sensor, a
pressure sensor and a Dean and Stark apparatus were placed
4134.7 g (26.13 mol) of nonanoic acid and 3061.0 g (9.42
mol) of mixed C14/16/18 alkylphenol. The mixture was
stirred and purged with nitrogen and subsequently 46.27 g
(0.48 mol) of methanesulphonic acid was added. The
pressure in the reactor was lowered to 82-77 mbar and the
contents of the flask were heated to 166-170°C. After 3

- 21 -

hours 150 g of water was collected in the Dean and Stark
trap. After about 8 hours the nitrogen pressure was
raised to 1 bar and the mixture was continuously purged
with nitrogen and allowed to cool to room temperature
overnight. The excess of nonanoic acid was removed by
passing the product twice through a wiped film evaporator
at 150°C, 0.1 mbar. Subsequently, the product was rolled
for 1.5 hr with 92 g of basic alumina and filtered to give
4300 g (95% yield) of mixed C14/16/18 alkyphenyl
nonanoate.

Example 22 - C14/16/18-alkylphenyldodecanoate

This was prepared using a procedure analogous to that
of Example 19, from the appropriate starting materials.

Example 23

The properties of the products of Examples 17, 18 and
20 to 22 were analysed in respect of i) the kinematic
viscosity at 100 °C (Vk100); ii) viscosity index (VI);
iii) pour point (PP); iv) volatility (as measured by
ThermoGravimetric Analysis); v) oxidation stability (as
measured by Differential Scanning Calorimetry); seal
swell; and deposit formation (as measured by the Wolf
Strip Test method). Besides, the products have been
compared with two commercial esters: BISOFLEX TOT,
tradename for a 2-ethylhexyl trimellitate; and PRIOLUBE
3939, a tradename for an ester of pentaerythritol and C_{5-9} linear acid.

Table 1 shows the physical properties of the
alkylphenol esters of the present invention as compared
to the commercially available products.

The Vk100 of an oil is measured under low shear
conditions (gravity). The viscosity index (VI) is a
number indicating the effect of change of temperature on
the Vk of an oil. A high VI signifies relatively small
change of Vk with temperature, which is desirable. The
Vk100 was determined according to ASTM D 445-94; the VI

was calculated according to ASTM D 2270-86.

The pour point is defined at the lowest temperature at which an oil will flow when cooled at a specific rate. In crankcase use, a low pour point is desirable. Pour point has been determined according to ASTM D 97-87.

The oxidation stability of the alkylphenol esters was evaluated by DSC. DSC measures the differential heat flow when a sample of oil in a small pan and an empty pan (reference) are heated under an oxygen or air atmosphere in a closed cell. Typically, a 2 mg sample of oil is used in an open aluminium pan. The measurements were designed to mimic oil conditions encountered in automotive engine lubrication. In temperature programmed (dynamic) experiments, the test temperature was increased linearly from 40 to 350 °C at 20 °C/min. The cell atmosphere was 205 kPa O_2, and the gas flow rate 60 ± 10 ml/min. The onset of rapid oxidation is marked by a rapidly increasing exotherm. The extrapolated onset temperature is defined by the intersection of the tangent at the steepest part of the increasing exotherm and the baseline extrapolated from lower temperatures, on a plot of power versus temperature. For neat fluids, a DSC onset temperature value above about 220 °C is considered good.

Weight loss up to 262 °C was determined according to method IP 393/91 from the record of mass loss as a function of temperature in a suitable ThermoGravimetric instrument, run at a constant heating rate of 10 °C/min from 40 to 550 °C under flowing nitrogen. This measurement has been shown (based on a limited correlation exercise) to provide an indication of the evaporative loss (= volatility) from an oil held at 250 °C (the "Noack method"). A low volatility (low volatile loss at high temperature) is desirable.

Seal swell was evaluated according to test method IP 278/72. A value of 9, as found for a 80:20 w/w blend

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of a commercially available synthetic base oil (referred to hereinafter as the reference oil) and PRIOLUBE 3939, is acceptable, but a lower seal swell is most desired to reduce wear.

5   The Wolf Strip Test (based on method DIN 51392) is an inclined hot plate test, where the lubricant under test is circulated at 50 ml/min. for a number of hours over a hot metal test strip, that is 8° declined against the horizontal. The ester was tested either neat or at 20%

10   w/w in a hydrogen base oil. The weight of deposit remaining on the test strip is recorded at the end of the test. A low deposit is desirable.

Table 1

Properties	Cpd of Example 17	Cpd of Example 18	cpd of Example 20	cpd of Example 21	cpd of Example 22	PRIOLUBE 3939	BISOFLEXTO T
VK100 (cSt)	5.5	6.3	4.73	5.01	5.96	4.9	8.4
VI	131	140	125	130	142	143	50
Pour point (°C)	-30	-15	-36	-33	-18	-57	-30
TGA (%)	2.8	1.5	nd	nd	3.2	4.0	4.2
DSC (°C)	225	217	nd	nd	237	210	218
Seal swell	7.3	2.6	nd	nd	nd	27	31
Wolf strip (mg) (20% ester)	313	594	nd	nd	nd	777	160
neat	16-40	n.d.	nd	nd	nd	115	10-32

n.d. not determined

- 2: -

It will be apparent to the skilled reader that the
alkylphenol esters not only exhibit the desirable
combination of low viscosity with low volatility, but
also exhibit a low seal swell and perform well in the
5   Wolf Strip Test.

Example 24

A C_{14-18}-alkylphenyl dodecanoate, the compound of
Example 22, was tested in a fully formulated oil for
diesel applications. The alkylphenol ester, at either 30
10   or 60% w/w concentration, was blended with the reference
oil used previously and detergent and ash levels in the
mid range of current commercially available diesel engine
oils.

Oxidation stability of the blend containing the
15   alkylphenol ester was tested by comparing the induction
periods during isothermal Differential Scanning Calori-
metry with blends containing a commercial polyol ester.
The IP was measured at 200 and 210 °C. Long IP's are
preferable. The test results are set out in Table 2.
20   These test results show that the alkylphenol ester at 30%
concentration shows an oxidation stability benefit over
similarly formulated synthetic base fluids, containing
either polyol esters (PRIOLUBE 3939 and 3970, ex
UNICHEMA), a trimellitate ester (REOLUBE OTM, ex FMC) or
25   a carbonate ester (AGIP MX2201, ex AGIP Petroli/ENICHEM
AUGUSTA JV) at equivalent concentrations at both 200 and
210 °C. The alkylphenol ester at 60% concentration shows
a twofold increase in induction period compared with the
blend of reference oil containing the same detergent and
30   ash levels and an appreciable benefit compared with the
commercial carbonate ester.

Table 2, induction periods by Isothermal DSC

Composition	at 200 °C/min	at 210 °/min
reference oil	14	8
30% alkylphenol ester	22	12
30% PRIOLUBE 3939	19	8
30% PRIOLUBE 3970	17	9
30% REOLUBE OTM	18	9
30% AGIP MX2201	20	10
60% alkylphenol ester	28	14
60% AGIP MX2201	23	9

Example 25

The 60% w/w lubricating oil composition of Example 24 was subjected to a caterpillar micro oxidation test, which is a laboratory bench text used to predict the lubricant deposit-forming tendencies under thin film conditions. Accordingly, samples are subjected to 230 °C under air with a set flow rate to oxidize oil and cause deposit-formation on a pre-weighed metal coupon. Deposits are then weighed and the accumulation of deposits determines the induction time. An induction period of 275 minutes was found, as compared to 115 minutes for the reference oil.

Example 26

An MWM-B Diesel Engine test (pursuant test method CEC L-12-A-76) was conducted to evaluate the 60% w/w lubricating oil composition of Example 24 as crankcase oil in respect of piston deposits and ring sticking. The higher the piston rating, the better the composition's performance. As may be learned from Table 3, the alkylphenol ester at this concentration dramatically improves the cleanliness ratings in many piston regions and in particular the top groove (i.e., groove 1), land 1 and undercrown as compared with the reference oil.

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Table 3

Lubricating oil composition	reference oil	60% alkylphenol ester
Groove 1	0.7	16
Land 1	64.3	81.5
Groove 2	94.9	95.1
Land 2	93.0	89.5
Groove 3	100	98.3
Mean	70.6	76.9
undercrown	65	79

Example 27

Use of high concentrations of polar esters in lubricants may cause problems of compatibility with elastomer sealing materials. The acrylate seal compatibility of the phenolic ester of Example 21 was tested according to test method CEC-L-39-T-87. The ester was tested at a concentration of 35% w/w in a polyalphaolefin-based engine oil containing a typical additive package, in comparison with corresponding oils where the base fluids was polyalphaolefin alone, or polyalphaolefin containing 35% w/w of an alternative commercially available aliphatic ester or diester. Results are shown in Table 1a.

Table 1a

Acrylate seal compatibility of engine lubricants containing esters at 35% w/w

Poperty	Required Limits	None	Polyol ester X	Polyol ester Y	diester Z	cpd of Example 21
				Ester		
Tensile strength (%)	-15 to +10	-11	-15	-23	-21	-9
Elongation (%)	-35 to +10	-37	-25	-22	-33	-19
Volume change (%)	-5 to +5	+1.9	+7.6	+14	+5.5	+4.8
Hardness (pts.)	-5 to +5	+4	-3	-9	-1	-4

Only the oil containing phenolic ester Example 21 passes all specification limits.

Example 28

Alkyl phenol esters similar to those of formula I but
with a smaller alkyl substituent of the phenyl ring, were
prepared by a carbonylation process analogous to that
described in Examples 17 and 18, and their kinematic
viscosity at 100°C (Vk 100) viscosity index (VI), pour
point (PP) and volatility (TGA) were investigated.
Details and results are given in Table 4, below, in which
R_1 and R_2 in the formula II are alkyl groups having the
specified number of carbon atoms.

(II)
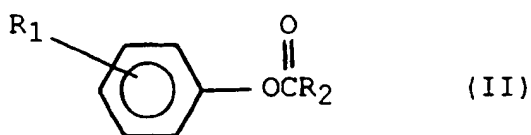
Table 4

Compound	R_1	R_2	VK100 (cSt)	VI	PP	TGA
A	8	8	2.84	82	-57	30.5
B	8	18	5.75	153	+18	1.8

It can be seen that unsuitable viscosity, VI, and
volatility are given where R_1 and R_2 each have 8 carbon
atoms. Increasing the number of carbon atoms in alkyl
group R_2 improves the viscosity, VI and volatility
favourably but increases the pour point to an
unsatisfactory level.

From Table 1 hereinbefore, it can be seen that all
the compounds of the formula I exemplified show in
comparison a very desirable combination of low
volatility, low viscosity, and low pour point with a high
VI.

C L A I M S

1. A process for the carbonylation of ethylenically unsaturated compounds by reaction thereof with carbon monoxide and a coreactant in the presence of a catalyst system obtainable by combining (a) a source of a Group VIII metal cation (b) a phosphine, arsine or stibine compound acting as a ligand; and (c) a source of anions, other than halide anions, carried out in the presence of substoichiometric amounts of a halide anion and/or -in case of a coreactant other than an aromatic alcohol- in the presence of a phenolic promoter.

2. A process as claimed in claim 1, carried out in the presence of a chloride or iodide anion.

3. A process as claimed in claim 1 or 2, carried out in the presence of a halide anion in a molar ratio versus the Group VIII metal cation that is less than 3:1, preferably less than 1:1.

4. A process as claimed in any one of claims 1 to 3, carried out in the presence of the phenolic promoter in an amount up to 40% by weight, preferably of 10 to 20% by weight, based on the total weight of reactants.

5. A process as claimed in any one of claims 1 to 4, wherein the Group VIII metal is palladium.

6. A process as claimed in any one of claims 1 to 5, wherein the phosphine, arsine or stibine compound is a bidentate ligand, containing a second atom that coordinates with the cation, selected from trivalent N, P, As or Sb atoms.

7. A process as claimed in claim 6, wherein the bidentate ligand is a compound of the formula $R^1R^2M^1-R-M^2R^3R^4$, wherein M^1 and M^2 independently are P, As or Sb, R represents a bivalent substituted or unsubstituted bridging group containing from 1 to 5 atoms

in the bridge, R^1 and R^2 together are a substituted or
unsubstituted bivalent group whereby the two free
valencies are linked to M^1, and R^3 and R^4 together are a
substituted or unsubstituted bivalent group whereby the
two free valencies are linked to M^2 or R^3 and R^4
independently are substituted or unsubstituted
hydrocarbyl groups.

8.   A process as claimed in claim 7, wherein the bivalent
(substituted) group, represented by R^1 together with R^2
is a bivalent cyclic group selected from 1,4-cyclo-
hexylene, 1,4-cycloheptylene, 1,3-cycloheptylene,
1,2-cyclooctylene, 1,3-cyclooctylene, 1,4-cyclooctylene,
1,5-cyclooctylene, 2-methyl-1,5-cyclooctylene,
2,6-dimethyl-1,4-cyclooctylene and 2,6-dimethyl-1,5-
cyclooctylene groups.

9.   A process as claimed in claim 6, wherein compo-
nent (b) of the catalyst system is selected from the
[3,3,1] and [4,2,1] isomers of 1,2-P,P'-bis(9-phospha-
bicyclononyl)ethane, 1,2-P,P'-bis(dimethyl-9-phospha-
bicyclononyl)ethane 1,3-P,P'-bis(9-phospha-
bicyclononyl)propane, and 1,3-P,P'-bis(dimethyl-9-
phosphabicyclononyl)propane.

10.   A process as claimed in any one of claims 1 to 9,
wherein the coreactant is an alkylphenol having one or
more alkyl groups of up to 30 carbon atoms attached to
the phenol molecule.

11.   An alkylphenol ester of the general formula

$$R'_n C_6 H_{(5-n)} OC(=O)R'' \qquad (I)$$
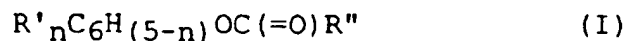
wherein R' is an alkyl group of from 10 to 30 carbon
atoms, n is an integer of 1 to 5, and R'' is an alkyl
group of from 1 to 30 carbon atoms.

12.   An alkylphenol ester as claimed in claim 11, wherein
R' is an alkyl group of from 12 to 20 carbon atoms.

13.   An alkyl phenol ester as claimed in claim 11 or claim
12, wherein R' is an alkyl group having at least 14 carbon

atoms.

14. An alkyl phenol ester as claimed in any one of claims 11 to 13, wherein R" is an alkyl group of from 4 to 22 carbon atoms.

15. An alkylphenol ester as claimed in any one of claims 11 to 14, wherein n is 1.

16. An alkylphenol ester as claimed in any one of claims 11 to 15, wherein R' together with R" have from 20 to 40 carbon atoms.

17. An alkylphenol ester as claimed in any one of claims 11 to 16, wherein the number of carbon atoms in R' is larger than or equal to the number of carbon atoms in R".

18. Use of the alkylphenol ester as claimed in any one of claims 11 to 17 as synthetic lubricant.

19. A lubricating oil composition comprising as base fluid an alkyl phenol ester as claimed in any one of claims 11 to 17.

20. A lubricating oil composition as claimed in claim 19, wherein the balance of the total base fluid is a base oil of mineral or synthetic origin.

A. CLASSIFICATION OF SUBJECT MATTER

IPC 6   C07C67/38   C07C69/017   C07C69/24   C10M105/34

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6   C07C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 94 18154 A (SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.) 18 August 1994 cited in the application see page 2, line 1 - page 3, line 32 see page 6 - page 7; examples 1-11 see page 10 - page 11; claims ---	1
X,Y	US 4 762 942 A (ALLAN WISSNER ET AL.) 9 August 1988 see column 23 - column 28; examples 29,37,45,53 ---	11-15,17
	-/--	

X	Further documents are listed in the continuation of box C.		X	Patent family members are listed in annex.

* Special categories of cited documents :

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Date of the actual completion of the international search	Date of mailing of the international search report
4 July 1997	1 5. 07. 97

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1

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT	
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